Emulsion-templated Porous Polymers Prepared by Thiol-ene and Thiol-yne Photopolymerisation using Multifunctional Acrylate and Non-acrylate Monomers

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Abstract

The chemical and mechanical properties of macroporous polymer substrates play a crucial role in the determination of their end-application. The preparation of highly (macro)porous monolithic polymers (polyHIPEs) by emulsion templating and thiol-ene/yne photopolymerisation, using multifunctional acrylate, allyl ether and alkyne-based monomers with trimethylolpropane tris (3-mercaptopropionate) (TMPTMP), is described in this work.

Issues associated with monomer solubility and/or stability of the produced high internal phase emulsions (HIPEs) are tackled. Scanning electron microscopy (SEM) is used to study the morphology and porosity (average void diameters) of the obtained materials. Due to the nature of the photoinitiated thiol-ene reactions, materials obtained from acrylate monomers display residual thiols that are quantified by a colourimetric (Ellman's) assay. Raman spectroscopy is also shown to be a complementary technique to evaluate the residual thiol content. The influence of the monomer functionality on the mechanical properties of the material is explored using compression tests. Significant differences in the surface functionality and mechanical behavior between materials prepared with comonomers able to homopolymerise (acrylates) and those unable to homopolymerise (allyl ethers; alkynes) are demonstrated.

Introduction

Macroporous polymers[1] have a wide range of potential applications, including in (bio)catalysis[2], gas storage[3], separation science[4] and tissue engineering[5]. They can be prepared by either templating or non-templating methods[6]. In non-templating approaches, phase separation or solvent evaporation can create a porous material from a single-phase precursor. Commonly employed non-templating methods for preparing porous polymers include thermally-induced phase separation and gas foaming. Due to its high degree of control over porosity, templating methods have gained much attention recently and have now become some of the most attractive methods of synthesising macroporous polymers[7]. Highly porous polymers can be prepared by the emulsion templating method, which involves the formation of a high internal phase emulsion (HIPE) followed by polymerization of its continuous phase. Once polymerised, the continuous phase of the HIPE contracts allowing droplets to connect with nearby droplets, leading to a fully interconnected, low density polymer foam – known as a PolyHIPE[3, 8-14]. The rapid curing time provided by photo-polymerisation allows the potential of synthesising polyHIPE materials from monomers which produce highly unstable emulsions[15-19].

Although thiol-ene (and thiol-yne) click chemistry has been employed extensively in recent years to prepare a wide range of novel materials[20-22], its application in the synthesis of macroporous materials has been reported only rarely. For example, thiol-ene and thiol-yne photopolymerisation were combined with microfluidics to prepare monodisperse macroporous polymer beads[23]. Thiol-ene photopolymerisation inside capillary columns was used to prepare monolithic stationary phases for capillary liquid chromatography[24, 25].

Enzymatic microreactors were produced by conducting thiol-ene photopolymerisations of emulsions inside microfluidic devices[26]. In 2011, Cameron *et al*. first introduced the preparation of well-defined polyHIPE materials by combining emulsion templating with thiol-ene and thiol-yne photopolymerization using a tri-acrylate and a bis-alkyne as comonomers[16]. Subsequent work explored the use of these materials as scaffolds for the *in vitro* culture of cells in 3D[27-30], and in the production of layered materials[31]. Acrylate-based monomers undergo homopolymerisation in addition to thiol-ene reaction, which results in residual thiols in the final material[32]. Residual thiols were found in thiol-acrylate polyHIPE materials prepared with different thiol:acrylate stiochiometries, even when the acrylate groups were in significant excess. For that reason, we sought to explore further the use of commercially available, non-acrylate comonomers with which to prepare polyHIPE materials by thiol-ene/yne photopolymerisation. Accordingly, we employed allyl ether-based comonomers (tetraallyl ether and diallyl ether) and an alkyne-based comonomer (1,7-octadiyne), in addition to a range of multifunctional acrylates, for polyHIPE preparation by photopolymerisation. We also undertook a thorough investigation of the morphology, surface functionality and compression behavior of the resulting materials. Compression data for methacrylate[33] and carbon black-filled[34] polyHIPEs have been reported previously, however, as far as we can tell, data for acrylate-, allyl ether- or alkyne-based polyHIPEs have not yet been reported. We show that non-acrylate monomers tend to give rise to an elastomeric material, whereas an acrylate counterpart produces a more rigid foam. It is also shown that non-acrylate comonomers give rise to very low levels of residual thiol groups.

Experimental

Materials

All chemicals were obtained from Sigma Aldrich apart from the surfactant Hypermer B246 (a block copolymer of polyhydroxystearic acid and polyethylene glycol), which was obtained from Croda International. All were used without further purification.

Methods

PolyHIPE preparation

In a 250 mL two-necked round-bottomed flask, an oil phase consisting of a 1:1 mixture (based on functional group stoichiometry) of monomers (trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) plus alkene or alkyne – see Scheme 1), 1,2-dicholorethane (DCE), surfactant Hypermer B246 and photoinitiator (a blend of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and 2-hydroxy-2-methylpropiophenone) was stirred continuously at ambient temperature using a D-shaped polytetrafluoroethylene (PTFE) paddle attached to an overhead stirrer at 350 rpm. An aqueous phase of deionised water was added drop-wise to the oil phase, with stirring, to form a HIPE with an internal (aqueous) phase volume fraction of 80%. The volumes of the monomers, DCE and deionised water used are given in Table 1. Once all the aqueous phase was added, the HIPE was either transferred immediately, or after stirring for a fixed time under ambient lighting in the

laboratory (Table 1), into a cylindrical PTFE mould (diameter 15 mm, depth 30 mm). The mould was secured between two glass plates and passed under a UV irradiator (Fusion UV Systems Inc. Light Hammer® 6 variable power UV curing system with LC6E benchtop conveyor and mercury discharge 'H' bulb) ten to fifteen times on each side, at a belt speed of 5.0 m/min., to ensure complete curing. The cured polyHIPE material was washed by immersion in acetone and then soxhlet extraction with dichloromethane for 24 h. The polyHIPE was then dried under reduced pressure at ambient temperature for 24 h.
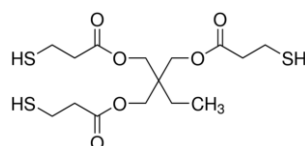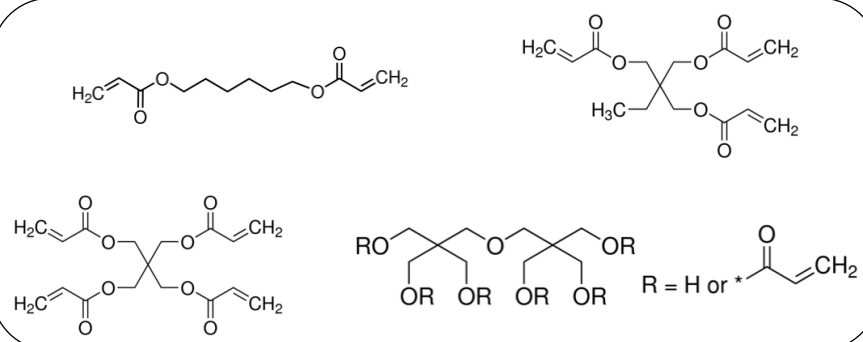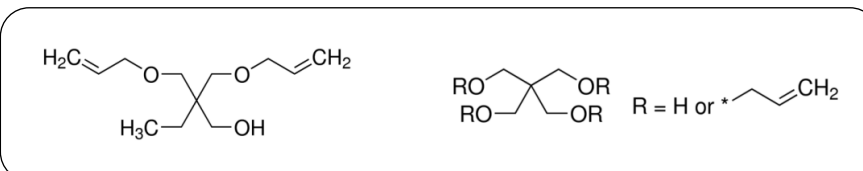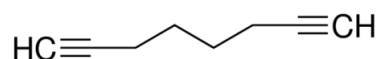
Scheme 1. Monomers used in this study. Thiol: trimethylolpropane tris(3-mercaptopropionate) (TMPTMP); acrylates (clockwise from top left): 1,6-hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), dipentaerythritol penta-/hexa-acrylate (DPEHA) and pentaerythritol tetraacrylate (PETA); allyl ethers (left to right): trimethylolpropane diallyl ether (TMPDAE) and pentaerythritol allyl ether (PEAE); alkyne: 1,7-octadiyne (ODY).

Characterisation

Scanning electron microscopy

PolyHIPE morphology was investigated using a Philips/FEI XL30 ESEM operating at 25 kV. Fractured polyHIPE pieces were sputter-coated with gold using a Bio-Rad E5400 sputter coating system and mounted on carbon fibre pads adhered to aluminium stubs. Average void diameters were then calculated using Image J Version 1.50i. One hundred voids were randomly chosen from an SEM image of the sample and the diameters measured. Void diameters measured in this way underestimate the true value as the voids are unlikely to be exactly bisected. Therefore a statistical correction factor was used to account for this underestimate[35].

Determination of residual thiol content using Ellman's reagent

Following a previously described method, the thiol loading of thiol–ene/yne polyHIPEs was

determined using a colourimetric assay[32]. Briefly: 5–10 mg polyHIPE was frozen in liquid nitrogen and then ground to a powder with a mortar and pestle. The polyHIPE powder was then transferred to a 5 mL volumetric flask containing 1 mL of THF. The polyHIPE was left to swell for 15 minutes. A solution of Ellman's reagent (1 mL, 5 µmol) in ethanol was prepared which was then added to the polyHIPE along with 5 µL of diisopropylethylamine. The flask was then shaken for 1 minute and then diluted to 5 mL with ethanol. The solution was then filtered and the absorbance of the filtrate was measured at 412 nm.

Raman spectroscopy

Raman spectra of dried polyHIPE samples were collected with a Renishaw InVia confocal micro-Raman system with an Ar ion laser (532 nm, approx. 300 mW) with the line focus fast-map option. The system was operated with the software WIRE 2.0. The samples were mapped without further sample preparation with a lateral step of 5 µm and a nominal line focus width of 1 µm. The spectral resolution of the obtain spectra was 1 cm^{-1}. 5% of the laser power and 10 seconds exposure time were adapted in these measurements.

Compression testing

The mechanical behavior of polyHIPE materials under compression was evaluated using a Shimadzu Autograph AGS-X Universal tester equipped with a 500 N load cell fitted with compression plates tested at ambient temperature. The polyHIPE samples were cylinders of

15 mm diameter and 20 mm height. Compression was continued until a final strain of around 80% was reached. Samples did not display any barreling up to this strain value. Experiments were repeated in triplicate using 3 different samples of each material to obtain average Young's modulus values.

Results and Discussions

Water-in-oil high internal phase emulsions (HIPEs) were prepared at ambient temperature by the slow addition of deionised water to the organic (continuous) phase, which contained comonomers, surfactant, organic solvent and photoinitiator, under constant mechanical stirring. A HIPE is defined as an emulsion where the internal (droplet) phase comprises more than 74% of the total emulsion volume. The HIPE internal phase volume fraction (ϕ) used in all preparations was 80% (Table 1). Following transfer to a mould, the formed HIPEs were cured by UV-initiated thiol–ene reaction[16].

Different multifunctional monomers, including acrylates, allyl ethers and a bis-alkyne, were reacted with trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) to produce a range of polyHIPE materials with different crosslinking densities (Scheme 1). HIPEs prepared from the comonomers TMPTA, PETA, DPEHA and ODY were found to be sufficiently stable at room temperature to enable curing by UV-initiated photopolymerisation, without any noticeable phase separation. Complete curing occurs in a matter of seconds, which allows relatively unstable HIPEs, such as those containing multifunctional thiols, to be used to prepare polyHIPEs. However, HIPEs formed from HDDA, PEAE and TMPDAE were found to

phase-separate rapidly once stirring ceased and before curing could occur, preventing the formation of well-defined porous materials. In the case of TMPDAE we attribute this to its higher hydrophilicity. The octanol-water partition coefficient, P, can be used to express the hydrophilicity of a molecule. Its logarithm (logP) is used routinely in pharmaceutical science to predict drug solubility. Experimentally, it is obtained by determining the concentration of a given substance partitioned between octanol and water phases. Thus, a lower logP value signifies a more hydrophilic molecule. The logP value of TMPDAE, calculated by a group contributions method [36], is 1.89 vs. 2.78 for TMPTA. This most likely arises from the former's hydroxyl group. For PEAE and HDDA, which are predicted to have similar logP values to TMPTA (2.90 and 2.88), the likely explanation for the lower stability is the presence of hydroxyl-containing impurities in the commercial monomer samples (the quoted purities are 70% and 80% respectively for PEAE and HDDA). To enhance stability, these HIPEs were subjected to extended mixing whilst under exposure to ambient light. This led to an increase in viscosity and hence the stability of the emulsion, presumably due to adventitious thiol-ene photopolymerization. The exposure time to ambient light required to allow successful HIPE formation was found to be very much case-dependent. Increasing the surfactant content and decreasing the solvent content for these HIPEs also improved stability.

Table 1. Composition of Thiol-ene/yne HIPEs and Ambient Light Exposure Times

Comonomer[a]	M_{com}[b]	M_{Surf}[c]	V_{solv}[d]	V_{aq}[e]	Exposure time[f]

	(g)	(g)	(mL)	(mL)	(min.)
TMPTA	2.96	0.47	7.0	56	—
PETA	2.65	0.41	7.0	54	—
DPEHA	2.85	0.47	7.0	62	—
HDDA	3.39	1.00	5.8	45	20
PEAE	1.92	0.44	5.3	42	40
TMPDAE	3.22	1.00	6.6	53	45
ODY	0.80	0.53	4.3	34	—

[a] see text for definitions; [b] mass of added comonomer to give 1:1 alkene/yne stoichiometry to TMPTMP; [c] mass of added surfactant; [d] volume of added DCE; [e] volume of added aqueous phase required to achieve ϕ=0.80; [f] time of exposure to ambient light prior to curing.

The morphology of polyHIPE materials plays a crucial role in determining their utility for a particular application. For example, polyHIPE scaffolds for 3D cell culture and tissue engineering are required to possess highly interconnected voids that allow cell migration into the scaffolds and free movement of nutrients and waste products to and from cells. TMPTA, PETA, DPEHA, PEAE, and ODY-based polyHIPEs all possess an interconnected network of pores as determined by SEM (Figure 1). The morphology and pore size distribution of polyHIPEs is determined by a combination of the emulsion droplet diameter at the gel point

and the rate of polymerisation. The droplet diameter is in turn determined by emulsion stability (assuming all emulsions are produced in an identical fashion). Polymerisation rate affects morphology because a slow polymerisation allows emulsion coarsening to take place before gelation, leading to a larger droplet diameter. The morphologies of polyHIPEs obtained from TMPTA, PETA and DPEHA (Figure 1A-C) show little variation from each other most likely because these monomers are very similar chemically (Scheme 1), and so their corresponding emulsions will have roughly the same emulsion stability and droplet diameter. ODY similarly gives rise to a stable emulsion which translates into the characteristic open-cell polyHIPE morphology (Figure 1E). As they are all acrylates, one can also assume that their rates of polymerisation will also be similar. PolyHIPEs made from HDDA and TMPDAE (Figure 1F, G) were more closed-cell in nature, presumably due to the lower stability of their emulsions, as discussed above. Curiously, PEAE, which also gives a relatively unstable HIPE, was able to produce a polyHIPE with a reasonably well-defined morphology (Figure 1D). At present we do not have a satisfactory explanation for this.
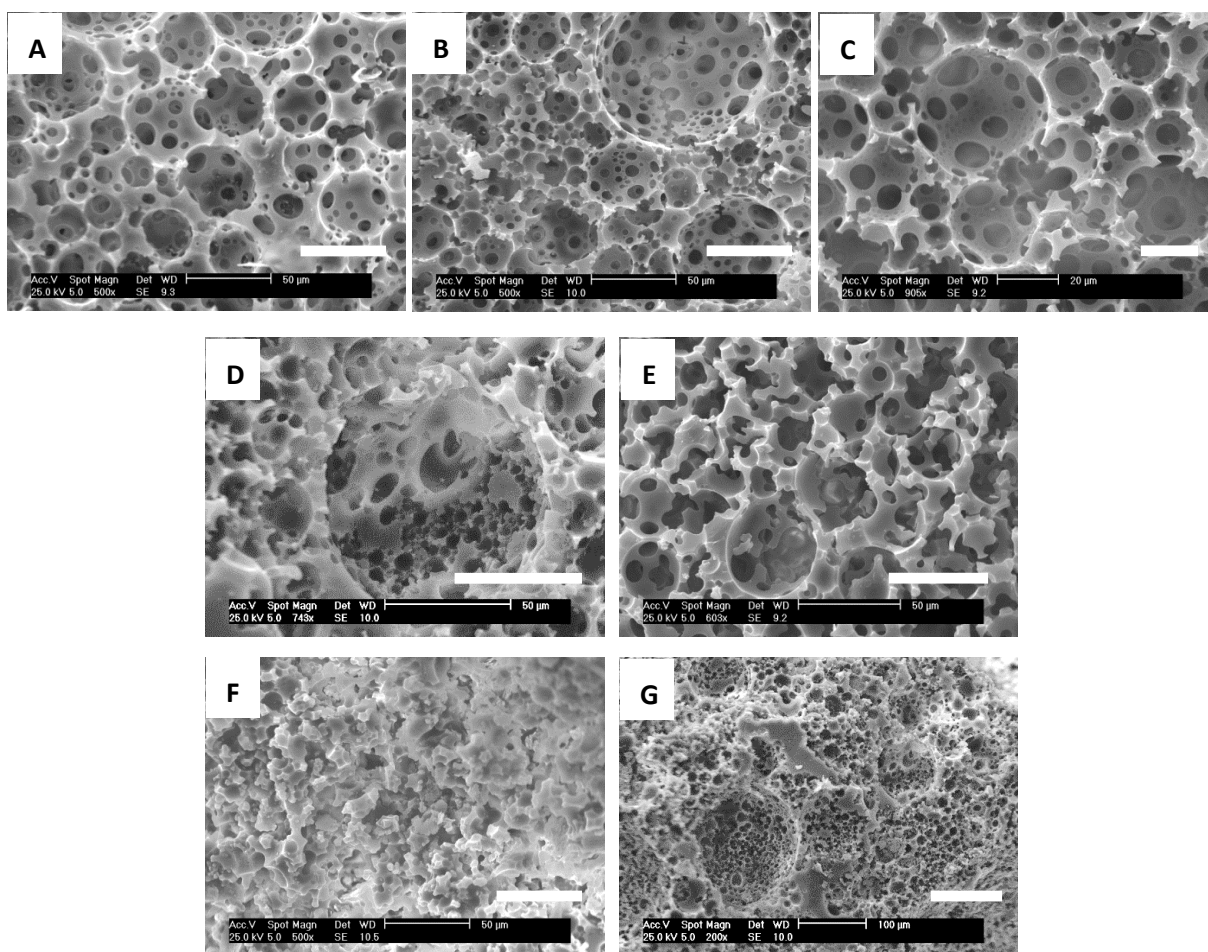
Figure 1. SEM images of thiol-ene/yne polyHIPE materials prepared with: A) TMPTA; B) PETA; C) DPEHA; D) PEAE; E) ODY; F) HDDA; G) TMPDAE. Scale bars: A), B), D), E), F) 50 μm; C) 20 μm; G) 100 μm.

Void diameter distributions for those materials that resulted in a well-defined open-cell polyHIPE morphology, namely those prepared from TMPTA, PETA, DPEHA, PEAE, and ODY, were determined by analysis of SEM images. The majority of voids in all cases were found to be in the range of 10-50 microns, similar to those prepared before by thiol-ene click chemistry (Figure 2). There does not seem to be a strong influence of monomer type on void

diameter for this set of 5 monomers.
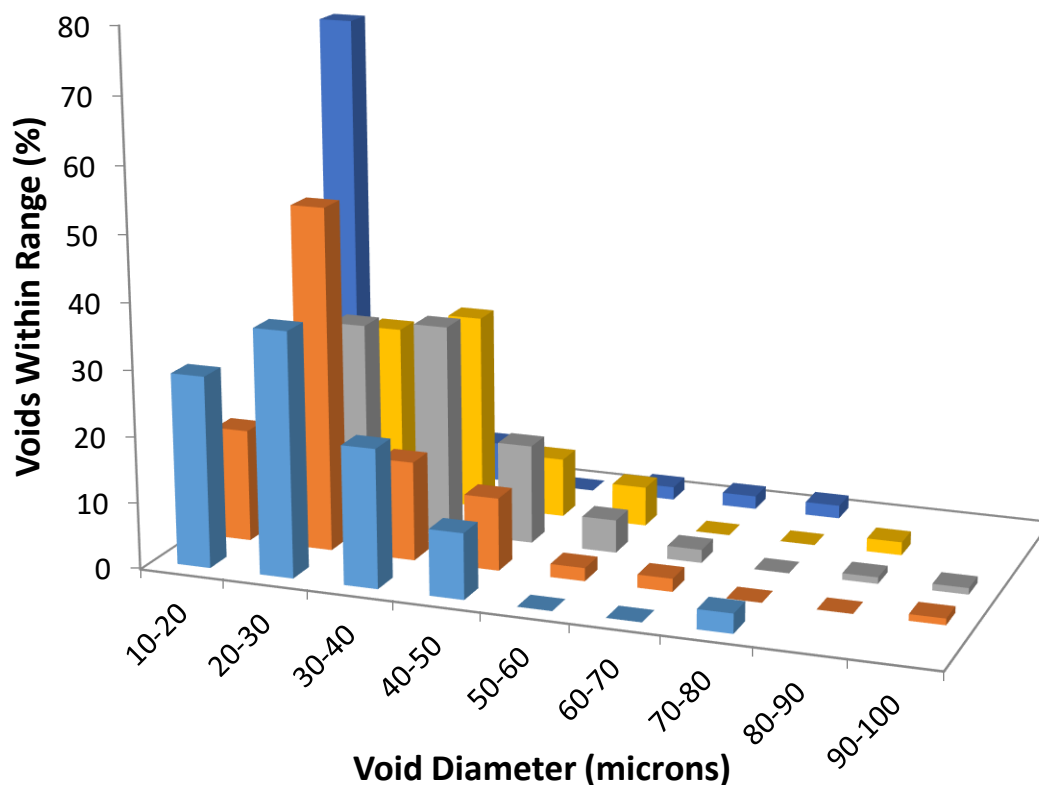
Figure 2. Void diameter distributions of polyHIPEs prepared from (front to back) TMPTA, PETA, DPEHA, ODY and PEAE, as determined by analysis of SEM images.

During UV irradiation of the HIPEs, there are two possible competing reactions: 1) the reaction between the thiol and the alkene/alkyne; and 2) the homopolymerisation of the (non-thiol) comonomer. Both reactions lead to network formation; however, the occurrence of homopolymerisation leads to unreacted residual thiols in the final material, since some of the alkene/yne groups are no longer available for reaction with thiols. The residual thiol

content in the polyHIPEs was quantified by a colourimetric (Ellman's) assay[32, 37]. This residual functionality can be used as a means by which thiol-ene polyHIPEs can be further modified chemically, by post-polymerisation reaction with acrylates[32]. In all cases, the thiol to ene/yne functional group ratio in the HIPE was kept constant at 1:1. Nonetheless, acrylate monomers led to polyHIPE materials with a significantly higher residual thiol content compared to those prepared from allyl or alkyne monomers. Acrylate monomers are prone to homopolymerisation under UV irradiation, while allyl and alkyne monomers do not undergo significant homopolymerisation under these conditions. Homopolymerisation consumes some of the acrylate monomers, shifting the stoichiometry away from 1:1 in favour of the thiol component. This in turn results in materials with residual unreacted thiols. Table 2 summarises the residual thiol content in the different polyHIPE materials prepared.

Table 2. Quantification of Residual Thiols in PolyHIPE Materials

Monomer category	Acrylate				Non-acrylate		
Comonomer	HDDA	TMPTA	PETA	DPEHA	PEAE	TMPDAE	ODY
Residual SH (mmol/g)	0.167 ±0.008	0.065 ±0.003	0.086 ±0.010	0.125 ±0.004	0.040 ±0.002	0.027 ±0.002	0.019 ±0.004

The presence of residual thiol groups in the polyHIPE materials can be identified qualitatively using Raman spectroscopy, which can be used to corroborate the Ellman's assay results. The

Raman spectrum of TMPTA-based polyHIPE shows a peak at around 2600 cm^{-1}, corresponding to residual thiol functionalities (Figure 3). This peak is not observed in the Raman spectra of PEAE and ODY-based polyHIPEs. The Ellman's assay results (Table 2) suggest lower but quantifiable levels of residual thiol for PEAE and ODY polyHIPEs. Close inspection of Figure 3B suggests that there is possibly a weak –SH signal (highlighted by *), whereas Figure 3C is devoid of any such minor peak. This agrees with the –SH contents revealed by Ellman's assay: 0.04 mmolg^{-1} for PEAE and 0.019 mmolg^{-1} for ODY. It is presumed that the residual thiols in the ODY material are below the resolution limit of the Raman technique.
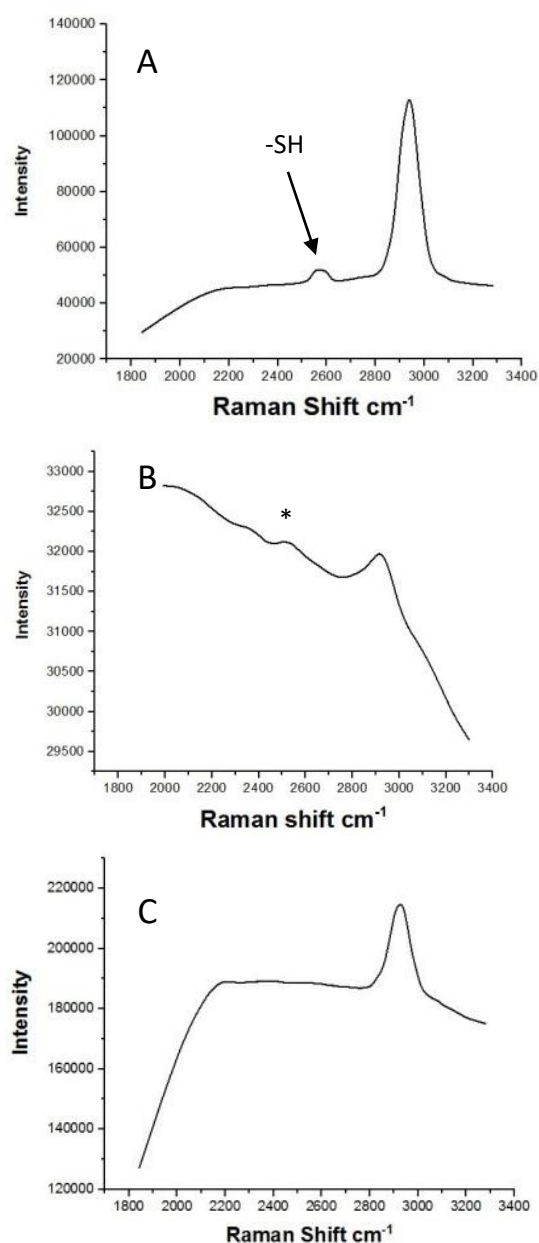
Figure 3. Raman spectra of thiol-ene/yne polyHIPE materials: A) TMPTA; B) PEAE; C) ODY. * in

B) indicates possible –SH signal.

Compression tests were performed on all polyHIPE materials. The resulting stress-strain

curves are shown in Figure 4. Materials displaying classical rigid foam behavior have curves

with an initial linear elastic region followed by a plateau. At small strains, usually less than ca.

10 %, the linear elastic region has a slope equal to the compression (Young's) modulus. At higher loads, the foam cells (voids) begin to collapse under the applied load giving a stress plateau. From Figure 4 it can be seen that samples PETA, DPEHA and ODY display stress-strain curves typical of rigid foams. The yield strengths can be estimated from the onset of the plateau region and range from around 100-700 kPa (0.1-0.7 Nmm^{-2}). Sample DPEHA has the highest yield strength and so is able to tolerate a much higher load than the other polyHIPE materials. Samples HDDA, TMPTA, TMPDAE and PEAE all display behavior typical of elastomeric foams and so a yield strength cannot be determined.
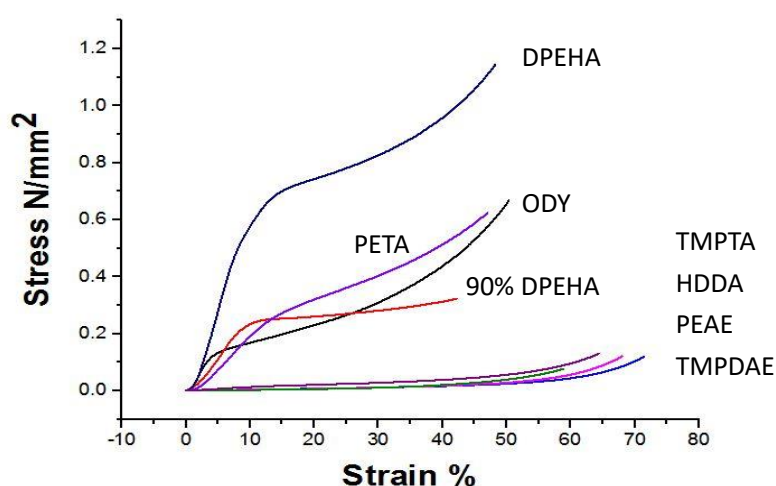

Figure 4. Compression stress-strain curves for thiol-ene/yne polyHIPE materials.

Table 3. Compression Data for Thiol-ene/yne PolyHIPE Materials

Comonomer	Young's modulus (kPa)			
	Sample 1	Sample 2	Sample 3	Average ± SD
HDDA	0.2	0.3	0.2	0.2 ± 0.06
TMPTA	1.0	1.0	0.9	1.0 ± 0.06
PETA	26.9	21.6	18.7	22.4 ± 4.00
DPEHA	90.9	84.5	77.4	84.3 ± 7.00
TMPDAE	0.5	0.3	0.3	0.3 ± 0.10
PEAE	0.5	0.3	0.4	0.4 ± 0.10
ODY	35.2	43.1	15.5	31.3 ± 11.6

Table 3 summarises the compressive (Young's) moduli values for all produced polyHIPE materials. The results show that the DPEHA-based polyHIPE is quite rigid, which can be attributed to the high functionality of DPEHA that leads to a highly crosslinked material. PolyHIPE materials made from monomers with levels of low functionality (HDDA and TMPDAE) were found to be flexible and could recover almost completely after compression, retaining their original dimensions (Figure 5).   The more rigid materials (PETA, DPEHA and ODY) showed significant irreversible deformation as a result of brittle crushing of the foam microstructure.
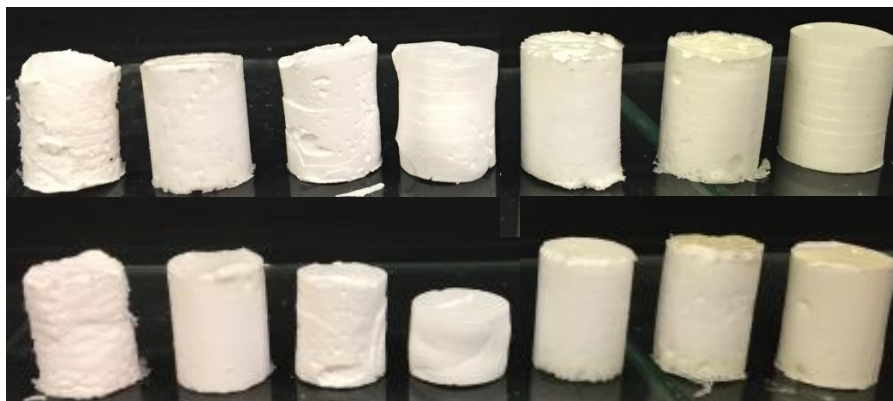
Figure 5. Images of polyHIPE materials before (top row) and 2h after (bottom row) compression testing. Comonomers (from the left): HDDA; TMPTA; PETA; DPEHA; PEAE; TMPDAE; ODY.

Conclusions

The preparation of a range of polyHIPE materials by emulsion templating and thiol-ene/yne photopolymerisation, using a tri-thiol (TMPTMP) plus a range of commercially available multi-functional monomers (acrylates, allyl ethers and a bis-alkyne), is described. For HIPEs that rapidly phase-separate after preparation, strategies to enhance stability to enable the successful production of homogeneous and well-defined polyHIPE materials are described. The pore (void) size distributions of the resulting materials were found to be the same, within experimental error. It has been demonstrated that acrylate monomers produce materials with significant levels of residual thiol functionality (up to 0.167 mmolg^{-1}) while

other comonomers have much lower levels of residual functionality. The mechanical behavior under compression of the materials has also been studied. PolyHIPEs ranging from highly elastic (Young's modulus = 0.2 kPa) to highly rigid (Young's modulus = 84.3 kPa) were produced. The mechanical behavior correlated with the degree of functionality of the monomer, more highly functional monomers giving higher levels of crosslinking and therefore a more rigid material. Thus, it can be seen that the surface chemistry and the mechanical behaviour of thiol-ene/yne polyHIPE materials can be tuned by judicious choice of alkene/yne comonomer.

Acknowledgements

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